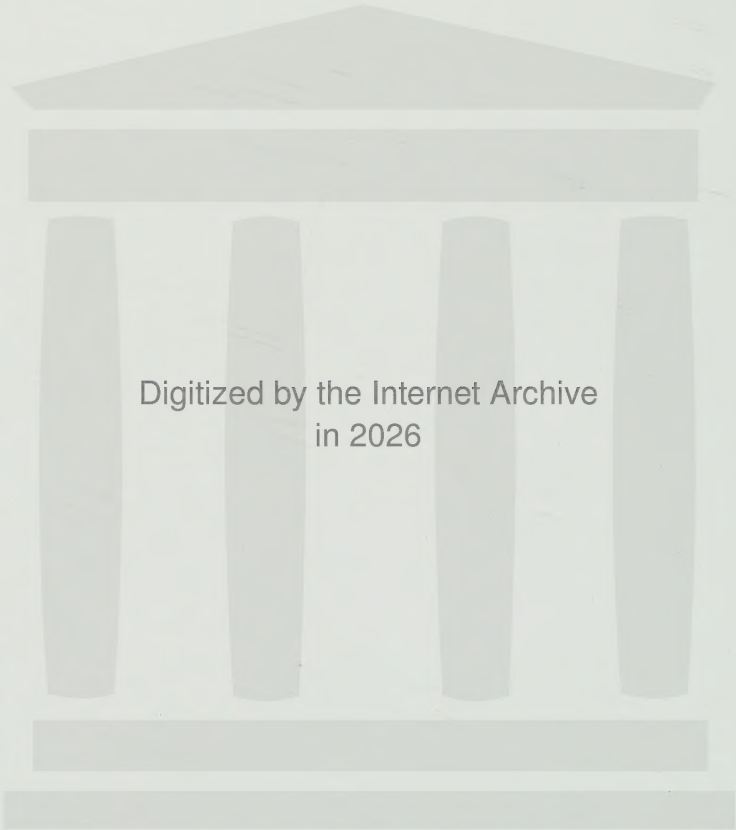
An Introduction to the Study of Qualitative Chemical Analysis

J. T. MCGILL


Digitized by the Internet Archive
in 2026

https://archive.org/details/introductiontost0000unse_j8a1

AN INTRODUCTION TO THE STUDY

OF

QUALITATIVE

CHEMICAL ANALYSIS.

BY

J. T. McGILL, Ph.D.,

Adjunct Professor of Chemistry in Vanderbilt University.

PRINTED FOR THE AUTHOR.
PUBLISHING HOUSE OF THE M. E. CHURCH, SOUTH.
J. D. BARBEE, AGENT, NASHVILLE, TENN.
1889.

PREFACE.

This little book is intended to be used only with the assistance of a teacher and as an introduction to some full work on qualitative analysis, such as that of Fresenius or Prescott.

Part I. contains such experiments as are found in late elementary works on inorganic chemistry. These experiments are designed to train the student in the construction and handling of chemical apparatus, and to teach him how to observe scientifically, reason upon his observations, and draw correct conclusions from them. They are selected for the most part with special reference to the analytical work that follows in Part II., and include the preparation of many of the reagents used in qualitative analysis and the examination of their properties. Part I. may be omitted by students who have taken a course in elementary chemistry, including experiments in the laboratory, such as Eliot and Storer's, Remsen's, or Williams's.

Part II. contains the special feature of this book—*i. e.*, the application to *qualitative analysis* of that method of teaching which, instead of imparting directly to the student the facts or laws which are the object of the study, leads him by questions and suggestions to work them out for himself. The use of this method for two years in Vanderbilt University has led me to conclude that it prevents to a great extent the blind following of directions, which the student is so liable to fall into in qualitative analysis, and that it also imparts greater interest to this study by requiring the student to test by practical examples the correctness of the conclusions which he has arrived at as the result of his own investigations. It is not expected that the student will be able thus to construct full analytical tables which

may be used for very delicate or extensive analysis; but he will become prepared to use such tables in works on qualitative analysis, not as a machine, but with an intelligent understanding of the principles involved.

In the selection and description of experiments I have used freely the works of Eliot and Storer, Remsen, Williams, Hart, and others.

The author would be glad to have the benefit of corrections or suggestions that may occur to any one who examines or uses the book.

Vanderbilt University, July, 1889.

SUGGESTIONS TO TEACHERS.

1. Have all material necessary for the exercise provided beforehand convenient in the laboratory.

2. Discuss in the class-room with the students the work of the last exercise; state the correct results and inferences, or assign the experiments when unsatisfactory for repetition, giving fuller instructions; give directions in regard to the experiments of the next exercise; make drawings on the blackboard of apparatus to be used, or better have a model of it at hand, and show how it is constructed; indicate the method of performing the experiments, but rarely perform the experiments yourself.

3. Caution the student in the use of dangerous chemicals and the performance of experiments in which accidents are liable to occur. In my experience more accidents have happened from the careless use of concentrated sulphuric acid than in any other way.

4. Require the pupils at the close of each exercise to deposit their note-books at some place where you can get them for examination. A case of "pigeon-holes" numbered to correspond with the numbers of the desks will be found convenient as a place of deposit for note-books, and, later in the course, for notes on analytical work and compounds for analysis.

DIRECTIONS TO PUPILS.

1. Before beginning an experiment read the directions through, and provide yourself with every thing which you can foresee to be necessary to complete the experiment.

2. Direct special attention to constructing neat and well-fitting apparatus, and keep every thing about your desk clean.

3. At the close of an experiment record in your note-book immediately (1) the material employed, a brief description of the apparatus used, the method of procedure; (2) what takes place; (3) the inferences you draw or what you have learned from the experiment.

4. Leave ample space in your note-book for making corrections and additions *without erasing any of the first record.*

EXPLANATIONS.

1. *Dilute* acid is intended unless *conc.* is prefixed.

2. When a formula is given without the name of the compound the name and formula will be found in some previous experiment.

3. An interrogation point inclosed in parentheses at the close of a statement means that the student is expected to determine by experiment whether the statement be true.

4. Weighed quantities of substances are used approximately, except when the expression "weigh out" occurs.

CONTENTS.

PART I. EXPERIMENTS IN GENERAL CHEMISTRY.

EXPERIMENT	PAGE
1. Length	9
2. Volume	9
3. Weight	9
4. The Bunsen Burner	10
5. Temperature of Ignition	10
6. The Blow-pipe and Blast-lamp	11
7. Charcoal as a Reducing Agent	11
8. Sodium Nitrate as an Oxidizing Agent	11
9. Heating on Asbestos; on Charcoal	12
10. Fusion on Platinum Wire; on Platinum Foil	12
11. Heating and Bending Glass	13
12 Evaporation, Distillation, Solution	13
13. Effect of Solutions upon Litmus	14
14. Dilute Acids	15
15. Ammonia	15
16. Hydrochloric Acid	16
17. Ammonium Chloride	16
18. Salts from an Acid and an Hydroxide	17
19 Decomposition of Mercuric Oxide	17
20. Oxides and Hydroxides of the Alkali Metals	18
21. Oxides and Hydroxides of the Alkaline Earth Metals	18
22. Oxides of Magnesium, Zinc, Tin, and Aluminium	19
23. Salts from an Acid and a Metallic Oxide	19
24. Sulphur	20
25. Oxides of Sulphur	20
26. Phosphorus Pentoxide	20
27. Sodium Sulphide	21
28. Iron Sulphide; Hydrogen Sulphide	22
29. Hydrogen by the Action of a Metal on Water	22
30. Hydrogen by the Action of a Metal on an Acid	23
31. Oxygen	24
32. Nitrogen	25

EXPERIMENT PAGE
33. Nitrous Oxide.... 26
34. Nitric Oxide.... 27
35. Nitric Acid.... 27
36. Hydrochloric Acid.... 28
37. Aqua Regia.... 29
38. Carbon Dioxide.... 29

PART II. EXPERIMENTS IN QUALITATIVE ANALYSIS.

THE METALS.

39. Separation of the Metals into Groups.... 31
40. Group I. Hydrochloric Acid Group.... 33
41. Group II. Hydrogen Sulphide Group.... 34
42. Group III. Ammonium Sulphide Group.... 37
43. Precautions in the Separation of Groups I., II., and III.... 40
44. Group IV. Ammonium Carbonate Group.... 40
45. Group V. Sodium Phosphate Group.... 42
46. Group VI. Soluble Group.... 42
47. Separation of Groups IV., V., and VI.... 43
48. Some Special Cases under Group III.... 44

THE ACIDS.

Inorganic Acids.

49. Barium Chloride Group.... 44
50. Silver Nitrate Group.... 45
51. Silicic Acid.... 45
52. Hydrofluoric Acid.... 46
53. Boric Acid.... 46
54. Sulphurous and Hyposulphurous Acids.... 46
55. Chloric Acid.... 47

Organic Acids.

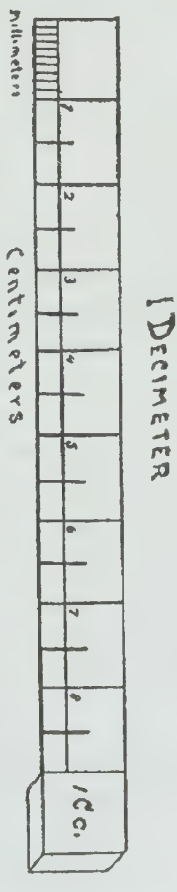
56. Test of an Organic Compound.... 47
57. Conc. Sulphuric Acid on Organic Acids.... 47
58. Oxalic, Tartaric, Citric, and Malic Acids.... 48
59. Succinic, Benzoic, Formic, and Acetic Acids.... 48
60. Organic Compounds Insoluble in Water.... 48

PART I.

EXPERIMENTS IN GENERAL CHEMISTRY.

LENGTH.

1. Estimate by the eye 1 dm. Close the book and lay off this distance on a slip of paper; divide it into cm.; divide 1 cm. into mm. Compare the scale you have made with the model. Repeat this experiment several times. Estimate the dimensions of glass tubing, test-tubes, etc.



VOLUME.

2. Pour 25 cc. of water into a small beaker. Mark the level of the water by means of a gummed label. Graduate a larger beaker to 100, 200, and 500 cc., and a test-tube to 5, 10, and 25 cc. Estimate the capacity of different vessels at your desk.

WEIGHT.

3. (*a*) Weigh the small graduated beaker. Pour into it 25 cc. of distilled water and weigh. Pour out the water, wipe the beaker perfectly dry, and weigh in it 25 cc. of conc. sulphuric acid. What is the specific gravity of conc. sulphuric acid? How many cc.

conc. sulphuric acid weigh 25 g ? How many cc. of alcohol, specific gravity 0.925, weigh 50 g. ?

(*b*) Balance two filter papers on the scales. Weigh out 1 g. of sodium chloride (common salt), 1 g. of lead chloride ($PbCl_2$), 1 g of calcium phosphate (Ca_3PO_4). By subdividing these, estimate the amount of each that would weigh 0.5 g., 0.1 g. Preserve the 1 g. weights of the above substances for future use.

THE BUNSEN BURNER.

4. (*a*) *Light and Heat of Flame*.—Examine the structure of a Bunsen burner. Compare the flame of the burner when the valve is open with the flame when the valve is closed. In which flame will a platinum wire glow more brightly? Which flame gives more light? which more heat? A deposit of carbon is made on a piece of porcelain held in one of these flames (?). Can you burn the carbon off? Rub together two pieces of charcoal so that a fine dust falls into the colorless flame. From the above experiments what inferences could you draw in regard to the causes of light and heat in flame?

(*b*) *Form of Flame*.—Make drawings of the flames of the Bunsen burner. Hold a platinum wire across the flame (try both flames) at different heights above the burner. Try a similar experiment with a splinter; with a glass rod. Thrust the sulphur end of a match quickly into the center of the flame. Hold a piece of paper horizontally in the flame and withdraw it just before it would ignite. Use wire gauze instead of paper, omitting the withdrawal. What do you learn from these experiments?

TEMPERATURE OF IGNITION.

5. Pour 1 cc. of carbon bisulphide (CS_2) into a porcelain crucible Can you ignite it by thrusting a heated glass or

iron rod into the mouth of the crucible? Bring the heated rod in contact with a little sulphur. Can you ignite coal gas with the heated rod? Suspend a spiral of platinum wire in a small flame above a burner. When the platinum is at a white heat put out the flame with a sudden puff of air. Explain the result. Lower a piece of wire gauze horizontally into the flame of a burner. Can you thus extinguish a small flame? Hold a piece of wire gauze horizontally three or four cm. above a burner; turn on the gas and try to light it above the gauze. If you succeed, gradually raise the gauze. What is the office of a wire gauze placed under vessels that are being heated?

THE BLOW-PIPE AND BLAST-LAMP.

6. Examine the structure of the blow-pipe; the blast-lamp Compare their flames with the burner flame. Practice with the blow-pipe until you can blow a steady stream of air for two minutes.

CHARCOAL AS A REDUCING AGENT.

7. Mix in a mortar 1 g. of lead carbonate with a sufficient quantity of powdered charcoal to nearly fill a small porcelain crucible. Cover the crucible and heat it over the blast-lamp for three minutes. Pour the contents of the crucible into a mortar, rub with water, pour off the charcoal and water and look for scales of lead in the bottom of the mortar.

SODIUM NITRATE ($NaNO_3$) AS AN OXIDIZING AGENT.

8. Fill a porcelain crucible half-full of $NaNO_3$ and heat until the salt fuses. Throw powdered charcoal in small quantities upon the fused mass. The charcoal is oxid-

ized, and burns, forming carbon dioxide gas. The chemical action that takes place may be expressed as follows:

Carbon (charcoal) and oxygen form carbon dioxide.

$$C + O_2 = CO_2.$$

Potassium nitrate (KNO_3) and potassium chlorate ($KClO_3$) are likewise used as oxidizing agents.

HEATING ON ASBESTOS; ON CHARCOAL.

9. (*a*) Place 0.1 g. of lead carbonate on a slip of asbestos, and heat it in the yellow or in the inner flame of the blow-pipe until a globule of lead is obtained. Heat the globule in the point of the blow-pipe flame. Oxide of lead is formed. Reduce the oxide to lead. Similar experiments may be tried with Zn, Sn, Cu, Sb, Bi, or their compounds.

(*b*) Try to reduce some of these compounds to the metallic state by heating them on a piece of charcoal before the blow-pipe. Is the reduction effected more easily on asbestos or charcoal?

FUSION ON PLATINUM WIRE; ON PLATINUM FOIL.

Borax, sodium metaphosphate, and sodium carbonate are often used as fluxes in heating substances on platinum wire, platinum foil, charcoal, or in crucibles. Nitrates of sodium or of potassium are sometimes used mixed with these. Platinum must not be used when the substance may be reduced to a metallic state.

10. (*a*) Make a transparent sodium metaphosphate bead in a loop on the end of a platinum wire, bring it while hot in contact with a small quantity of powdered manganese carbonate, heat in the oxidizing, then in the reducing flame of either the Bunsen burner or the blow-pipe. Observe the change in color. Try a similar experiment with a borax bead and cobalt carbonate.

(*b*) Mix 0.05 g. of manganese carbonate with 0.2 g. of sodium carbonate and heat on a platinum foil.

HEATING AND BENDING GLASS.

The operations should first be performed by the teacher in the presence of the class.

11. Round the ends of some glass rods in the hottest part of the flame of the Bunsen burner. Make half a dozen ignition tubes by melting in two at the middle pieces of glass tubing about 15 cm. long. Bend eight tubes at right angles, making six of them with the limbs 6 and 9 cm., one 25 and 10 cm., and one 35 and 8 cm. long. Round the sharp edges of the ends of these in the flame.

EVAPORATION, DISTILLATION, SOLUTION.

12. (*a*) Dissolve 1 g. NaCl in 20 cc. water. Evaporate half of the solution to dryness in a porcelain dish. What remains? Taste it. Distill the remainder of the solution, heating carefully until the distillate amounts to several cc. (The distillate is the part that passes over.) Evaporate the distillate to dryness. What remains? A convenient apparatus for this purpose may be made by connecting two large test-tubes by a tube 15 cm. long, curved so that the test-tubes set at about right angles to each other. A groove in the side of the stopper of the tube used to collect the distillate will permit the escape of uncondensed vapor.

(*b*) Place 0.1 g. powdered barium sulphate ($BaSO_4$) in a test-tube. Pour into the test-tube 1 cc. water. Does the $BaSO_4$ appear to dissolve? Add 5 cc. water, boil, and filter. Evaporate a portion of the filtrate—*i.e.*, the part that runs through. Is $BaSO_4$ soluble in water?

(*c*) Weigh out 0.1 g. calcium sulphate ($CaSO_4$). Shake it up with 5 cc. water, and let it stand a few minutes. If

it does not all dissolve, add more water, shake, and let it stand. Determine in how many times its weight of cold water $CaSO_4$ is soluble, 1 cc. water weighing 1 g. How could the exact solubility of $CaSO_4$ be determined without adding a sufficient amount of water to dissolve the whole of the weighed amount taken? Save 10 cc. of the solution for 12 (*e*) and 12 (*f*).

(*d*) Make a strong solution of 0.2 g. powdered crystalline lead chloride in hot water. Cool the solution. Explain the result. Does all of the lead chloride crystallize out?

(*e*) Add 10 cc. alcohol to 5 cc. $CaSO_4$ solution.

(*f*) Add 10 cc. alcohol to a strong solution of sodium chloride, filter, and dry the precipitate. Is it sodium chloride?

(*g*) Add conc. hydrochloric acid to a strong solution of sodium chloride, filter, and evaporate off the acid from the residue. What is this residue?

(*h*) The same as (*g*), using barium chloride instead of sodium chloride.

(*i*) Dissolve 1 g. of calcium phosphate (bone ash) in hydrochloric acid, and evaporate to dryness until the residue does not smell of acid. Is calcium phosphate attacked by the acid, or simply held in solution?

(*j*) Add solid sodium carbonate to 1 cc. hydrochloric acid until effervescence ceases. Is the gas that comes off combustible? Evaporate the solution to dryness. Compare the taste of the residue with that of the sodium carbonate. How does this solution differ from the preceding?

(*k*) Dissolve sodium carbonate in water, evaporate, and examine the residue.

EFFECT OF SOLUTIONS UPON LITMUS.

13. Test the reaction of all the solutions at your desk

to red and to blue litmus paper. Those turning blue to red are said to have an acid reaction, those turning red to blue an alkaline reaction, and those not changing the color of either red or blue litmus a neutral reaction.

DILUTE ACIDS.

14. (*a*) Pour 5 cc. conc. sulphuric acid into 25 cc. water. Notice the rise in temperature. This is the strength of the dilute sulphuric acid at your desk. Water must never be poured into conc. sulphuric acid. Why not?

(*b*) Pour 5 cc. conc. hydrochloric acid into 25 cc. water. This is the strength of the dilute hydrochloric acid at your desk.

(*c*) Pour 5 cc. conc. nitric acid into 25 cc. water. This is the strength of the dilute nitric acid at your desk.

(*d*) Dilute with water 5 cc. of each of the above solutions (*a*), (*b*), (*c*), to 500 cc., and compare the acidity by tasting.

AMMONIA.

15. (*a*) Distill some sodium hydrate solution. Test the distillate with litmus paper; the residue.

(*b*) Pour 25 cc. conc. ammonia into a small flask, through the stopper of which is inserted a straight glass tube 25 cm. long, open at both ends. Hang a test-tube or small flask over the end of the tube. Warm the ammonia. When the test-tube is full of the gas, which may be known by the smell of ammonia at its mouth, take it off, keeping its mouth downward, and dip the end of it under the surface of the water. Explain what happens. Is ammonia gas combustible? Is it lighter or heavier than air? What is the color of the gas? Is it more soluble in cold or hot water? Save 100 cc. of the gas in a closely-stoppered, inverted bottle for 17 (*a*). A gas is said to be collected by upward displacement when

collected as in this experiment. Ammonia gas has the formula NH_3. Its solution in water is called ammonia (also ammonium hydroxide and ammonium hydrate), and has the formula NH_4OH; but in reactions it is often written NH_3.

HYDROCHLORIC ACID.

16. Heat 25 cc. of conc. hydrochloric acid in a small flask under a hood. A gas is given off. Collect it by letting the outlet tube extend downward almost to the bottom of the receiving vessel which may be covered by a piece of paper. A piece of moistened blue litmus paper at the point where the outlet tube pierces the paper covering will indicate when the vessel is filled by turning red. The gas is thus collected by downward displacement. Fill several bottles and cover their mouths with watch-glasses or glass plates. Invert one of the bottles in water, and remove the glass covering. Is the gas more soluble in cold or hot water? Is it combustible? Is it lighter or heavier than air? Hydrochloric acid gas has the formula HCl. Its solution in water is called hydrochloric acid, or muriatic acid, and in reactions is also written HCl.

AMMONIUM CHLORIDE.

17. (*a*) Bring the mouth of the bottle of ammonia gas saved from experiment 15 over a bottle of hydrochloric acid gas, and mix the gases.

(*b*) Evaporate to dryness 10 cc. of ammonium chloride solution, and compare the residue with the solid product obtained by mixing hydrochloric acid gas and ammonia gas, (1) by tasting, (2) by heating on a piece of platinum foil.

(*c*) Suspend a drop of concentrated hydrochloric acid on the end of a glass rod, and bring it near the mouth of a bottle of ammonia What is the smoke that is formed?

Ammonia gas and hydrochloric acid gas form ammonium chloride.

$$NH_3 + HCl = NH_4Cl.$$

Bring a drop of the acid near a bottle of sodium hydroxide. (The hydroxides are also called hydrates.) Try the effect of ammonia gas on other acids in the same way, or by bringing a drop of conc. ammonia near the mouth of the bottle of acid.

SALTS FROM AN ACID AND AN HYDROXIDE.

18. (*a*) Mix till neutral to litmus paper dilute HCl with 10 cc. dilute NH_4OH. If too much acid be added, neutralize the acid by adding drop by drop *very* dilute NH_4OH. Evaporate the neutral solution to dryness; taste the residue; heat it to redness. The substance will be recognized as NH_4Cl. The reaction may be written thus:

$$NH_4OH + HCl = NH_4Cl + \overset{\text{Water.}}{H_2O}.$$

(*b*) Try some of the following experiments, and write the reaction for all of them: HCl neutralized with potassium hydroxide (KOH), with sodium hydroxide (NaOH); nitric acid (HNO_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), each neutralized with NH_4OH, KOH, NaOH, respectively. *By neutralizing an acid with an hydroxide a salt is formed.*

DECOMPOSITION OF MERCURIC OXIDE.

19. Heat 1 g of mercuric oxide (HgO) in a test-tube. Insert a glowing splinter into the mouth of the tube. The gas given off, which causes the glowing splinter to ignite, is oxygen. Mercuric oxide is decomposed by heating into mercury and oxygen. $HgO = Hg + O$. Oxygen was first obtained in this way. Some other oxides are decomposed by heating into the metal and oxygen.

OXIDES AND HYDROXIDES OF THE ALKALI METALS.

20. (*a*) Place in a small porcelain dish a piece of potassium the size of a pea. The change of color at the surface on remaining in the air is due to the formation of the oxide of potassium. (Are gold, silver, tin, zinc, iron oxidized thus?) Heat gently. The oxidation takes place more rapidly. After the potassium is completely oxidized allow it to cool, and then add a few drops of water. What causes the rise in temperature? Test the solution with litmus paper. What does the solution contain? $K_2O + H_2O = ?$

(*b*) Perform a similar experiment with sodium. $Na_2O + H_2O = ?$ The teacher should furnish for experiments in which they are required K, Na, and P already cut into pieces of the proper size.

OXIDES AND HYDROXIDES OF THE ALKALINE EARTH METALS.

21. (*a*) Is calcium carbonate ($CaCO_3$) soluble in water? Try a particle of it. Test the liquid with litmus paper. Heat 5 g. $CaCO_3$ in an open porcelain crucible over a blast-lamp for several minutes. $CaCO_3 = CaO + CO_2$.

Pour a portion of the contents of the crucible into a porcelain dish, and when that in the dish has cooled pour on it a little water. What causes the heat? Calcium hydroxide is formed: $CaO + H_2O = Ca(OH)_2$. Test with litmus paper. The solution of $Ca(OH)_2$ in water is called lime-water. Prove that $Ca(OH)_2$ is soluble in water. Is it more soluble than KOH or NaOH?

(*b*) Rub some moist $Ca(OH)_2$ with a particle of any ammonium salt. What is given off? Write the reaction. Heat moist $Ca(OH)_2$ with an ammonium salt. Ammonia gas for making ammonium hydroxide (ammonia) is thus manufactured. Will KOH or NaOH de-

compose an ammonium salt? How can you distinguish an ammonium compound from other compounds?

OXIDES OF MAGNESIUM, ZINC, TIN, AND ALUMINIUM.

22. Heat a platinum wire. There is no chemical change. Heat a magnesium wire. Tilt the burner to one side so that the magnesium oxide formed in the combustion may be caught in a dish. Moisten the oxide with water and test with litmus paper. Is it soluble in water? in hydrochloric acid? Does hydrochloric acid form a new compound with it or merely hold it in solution as in the case of calcium phosphate in 12 (*i*)? Is iron easily oxidized? Does oxide of iron part with oxygen so easily as HgO? Is it soluble in water? What would you say of ZnO, SnO_2, Al_2O_3 in these respects?

It is seen from experiments 20 and 21 that the oxides of the *alkali metals* and of the *alkaline earth metals* unite with water to form soluble hydroxides. The oxides of most of the other metals do not combine directly with water, but under certain conditions they form hydroxides almost insoluble in water. The hydroxides of the metals are called bases. They unite with acids to form salts (18).

SALTS FROM AN ACID AND A METALLIC OXIDE.

23 (*a*) Dissolve 1 g. of zinc oxide in dilute HCl. Evaporate to dryness. The residue is a salt soluble in water. $ZnO + 2HCl = ZnCl_2 + H_2O$. *By dissolving a metallic oxide in an acid a salt is formed.*

(*b*) Dissolve copper oxide (CuO) in H_2SO_4. Write the reaction. Evaporate till a drop of the solution placed on a watch-glass will deposit crystals on cooling Set the solution aside to cool.

(*c*) Heat in a crucible or dish 1 g. crystalline copper sulphate. $CuSO_4, 5H_2O = CuSO_4 + 5H_2O$.

SULPHUR.

24. (*a*) Heat slowly 15 g. S in a test-tube. Continue to heat until it boils, noting the changes which the S undergoes. Pour the melted S in a fine stream into a dish of water. Examine the S that has been poured into the water. Will it retain its plastic condition if kept under water? in the open air?

(*b*) Melt in a crucible or in a small beaker 25 g roll sulphur. Let it cool slowly and quietly. When a thin crust has formed on the surface, make a hole in the crust and pour out the liquid S. Examine the crystals that remain in the vessel.

(*c*) Pour 3 cc. carbon bisulphide (CS_2) upon 1 g S in a test-tube. Close the mouth of the test-tube and shake for a few moments. When the S has dissolved pour the solution into a watch-glass. Examine the crystals that form as the CS_2 evaporates.

(*d*) Add a few drops of conc HCl to 5 cc. ammonium sulphide. Sulphur separates from the liquid in a finely-divided state.

OXIDES OF SULPHUR.

25. Make a hollow in the end of a piece of chalk. Place in it some sulphur. Ignite the sulphur and suspend it in a large bottle. The odor is that of sulphurous anhydride formed by the oxidation of the sulphur. $S + O_2 = SO_2$. Pour some water into the bottle. Test the solution with litmus paper. SO_2 is an acid-forming oxide. The acid formed is sulphurous acid. $SO_2 + H_2O = H_2SO_3$. A higher oxide of sulphur (SO_3) forms with water sulphuric acid. $H_2O + SO_3 = H_2SO_4$.

PHOSPHORUS PENTOXIDE.

26. Repeat experiment 25, using instead of S a piece of *dry* phosphorus half the size of a pea. The white va-

por is phosphorus pentoxide (P_2O_5). With water it forms phosphoric acid. $P_2O_5 + 3H_2O = 2H_3PO_4$ What salt is formed by neutralizing this acid with NaOH? with $Ca(OH)_2$? Write the reactions

The oxides of most of the non-metallic elements are acid-forming oxides—*i. e.*, unite with water to form acids (25 and 26).

SODIUM SULPHIDE.

Sulphur forms many compounds analogous to those of oxygen. Recurring to experiment 20, perform the following experiments and write the reactions:

27. (*a*) Cover a piece of sodium in a porcelain crucible with sulphur, put on the crucible lid, and warm gently. When the crucible has cooled dissolve a portion of its contents in a few drops of water, reserving the remainder for 27 (*c*). Test the solution with litmus paper. The solution contains sodium sulphide (Na_2S). Place a drop of it on a silver coin The dark substance is silver sulphide (Ag_2S). Rub the spot with a little potassium cyanide. (Potassium cyanide is very poisonous) Add a few drops of the Na_2S solution to a solution of silver nitrate in a test-tube, then gradually add potassium cyanide solution.

(*b*) Try the effect of barium sulphate on a silver coin; of sodium carbonate Heat on charcoal before the blowpipe a mixture of sodium carbonate and barium sulphate. Test the melted mass as the product of sodium and sulphur was tested in 27 (*a*). How can the presence of sulphur be detected in an insoluble compound?

(*c*) Add HCl to the sodium sulphide reserved from 27 (*a*) until the solution is neutral to litmus. Compare with 18 and write the reaction. The gas given off is hydrogen sulphide (H_2S). What remains in solution?

IRON SULPHIDE; HYDROGEN SULPHIDE.

28. (*a*) Examine fine iron filings and powdered sulphur as follows: (1) With a magnifying-glass, (2) by bringing a magnet near them, (3) solubility in water, (4) solubility in carbon bisulphide, (4) solubility in acid

(*b*) Mix thoroughly 2 g. of iron filings with 2 g. of sulphur. Examine small portions of the mixture as in 28 (*a*).

(*c*) Pour the mixture into a dry test-tube, and heat till the mixture glows. When the glowing has ceased take out the mass, and examine small portions as in 28 (*a*).

(*d*) Put the remainder of the iron sulphide into a test-tube, add H_2SO_4, and test the properties of the gas. What remains in solution in the test-tube? Write the reaction. The solution of the gas in water is the hydrogen sulphide at your desk. The solution of ammonium sulphide at your desk is made by saturating a solution of ammonia with hydrogen sulphide gas, or a solution of hydrogen sulphide with ammonia gas.

(*e*) Try the effect of acids, dilute and strong, upon hydrogen sulphide solution; upon ammonium sulphide solution.

(*f*) Try the effect of a few drops of hydrogen sulphide on a solution of silver nitrate; lead acetate. Try ammonium sulphide on these solutions.

HYDROGEN BY THE ACTION OF A METAL ON WATER.

29. (*a*) Throw a piece of potassium the size of a grain of wheat on water. Notice the color of the flame. What burns? Test the water with litmus paper.

(*b*) Throw a piece of sodium as large as a pea on some water in a porcelain crucible. Wrap a piece of sodium in a piece of thin paper and throw it on the water in the crucible. Test the water with litmus paper. Evaporate

to dryness and compare the residue with that obtained by evaporating some solution of sodium hydroxide. Neutralize with HCl. What is formed? Did the sodium get oxygen from the air in burning on the water?

(*c*) Fill a test-tube with water and invert it in a dish of water. Take care that no bubble of air remains in the tube. At the close of the experiments with hydrogen (30) explain the reason of this precaution. Now take a small piece of dry sodium on the point of a rat-tail file and thrust it under the mouth of the test-tube so that the sodium will rise in it. Close the mouth of the test-tube with the thumb, and open it near a flame. The gas that burns is hydrogen. Test the water in the dish with litmus paper. What elements does this experiment prove water to contain?

Water is decomposed by iron at a high temperature. Water may be decomposed by a current of electricity, and the volume of hydrogen and oxygen measured. The volume of the hydrogen is then found to be twice that of the oxygen. The action of an acid on a *metallic oxide* has been found to result in the formation of a salt and water (25)—*e. g.*, $ZnO + H_2SO_4 = ZnSO_4 + H_2O$. Let us try the effects of an acid on a *metal.*

HYDROGEN BY THE ACTION OF A METAL ON AN ACID.

30. Pour H_2SO_4 on some pieces of Zn in a small flask or large test-tube. Collect the gas over water in test-tubes at first, and ignite the gas as in 29 (*c*). What do you infer from the way the gas first collected burns? What precautions must be observed in making this gas? When the gas has been coming off for several minutes, and when collected in a test-tube is found to burn quietly, collect several bottles of the gas and try the following experiments:

(*a*) Thrust a lighted taper into a bottle of the gas held mouth downward (why not mouth upward?), withdraw the taper; insert again while the gas is burning.

(*b*) Fill a small bottle with air and hydrogen in the proportion of three to one by volume. Let the mixture stand for awhile, and then bring the mouth of the bottle near a flame How could hydrogen be emptied from one vessel into another in the air? under water? Could hydrogen be collected by downward displacement in the air? by upward displacement? Why not collect it thus instead of over water? Why can you not collect ammonia gas or hydrochloric acid gas over water?

(*c*) Arrange an apparatus for burning hydrogen in a jet. Does the flame afford much light? much heat? What is formed in the combustion? Hold a dry beaker over the hydrogen jet. What is deposited on the inner surface of the beaker? What remains in solution in the flask after making the hydrogen? Write the reaction. Can other metals and other acids be used in making hydrogen? Try several in test-tubes. *By dissolving a metal in an acid a salt is formed.*

OXYGEN.

We have seen that mercuric oxide when heated decomposes into mercury and oxygen: $HgO = Hg + O$. Oxygen can be made also by heating some other oxides rich in oxygen. Black oxide of manganese (MnO_2) when heated decomposes as follows: $3MnO_2 = Mn_3O_4 + O_2$. Oxygen is generally made by heating potassium chlorate ($KClO_3$) By mixing with the $KClO_3$ some MnO_2 or Fe_2O_3 the oxygen comes off at a lower temperature and more regularly. The MnO_2 should be heated to redness to insure the destruction of any impurity of organic matter before using it to mix with $KClO_3$.

31. Mix about equal weights of $KClO_3$ and MnO_2. Fill a test-tube about one-third full of the mixture, heat and collect the gas over water, and try the following experiments:

(*a*) Plunge the glowing end of a splinter into a bottle of oxygen.

(*b*) Fasten a piece of charcoal to a large iron wire, heat it to redness, and lower into a bottle of oxygen.

(*c*) Ignite some sulphur placed in a hollowed crayon, and lower it into a bottle of oxygen.

(*d*) Same as (*c*), substituting a piece of *dry* phosphorus for sulphur.

(*e*) Same as (*c*), substituting a piece of sodium for sulphur.

(*f*) Attach a net of fine iron wire to the end of a large iron wire, heat to redness, and plunge quickly into a bottle of oxygen

What are formed in the above combustions? Pour a little water into the bottles in which the combustions have been made, and test the reaction with litmus paper. After the test-tube in which the mixture was heated has cooled, pour some water into it, warm, and filter. Add a few drops of silver nitrate solution to a portion of the filtrate. Add a few drops of silver nitrate solution to a solution of $KClO_3$. The change which the $KClO_3$ has undergone is expressed by the equation $KClO_3 = KCl + 3O$.

The reaction with nitrate of silver is as follows: $KCl + AgNO_3 = KNO_3 + AgCl$. AgCl is insoluble in water. Is it soluble in HNO_3? Will other chlorides in solution give a precipitate with $AgNO_3$?

NITROGEN.

32. (*a*) Float a small porcelain crucible on the surface of some distilled water in a large dish. Dry by means

of filter paper a piece of phosphorus half the size of a pea, and place it in the crucible. Set fire to the phosphorus and lower over it carefully a large-mouthed bottle. When the P_2O_5 fumes produced by the combustion have been absorbed by the water, mark with a label the level of the water in the bottle. The gas remaining in the bottle is nitrogen. Close the mouth of the bottle, and take it out of the water.

(*b*) Pour some clear lime-water into the bottle, and shake it up with the nitrogen. Does nitrogen render lime-water milky? Is nitrogen combustible? Does it support combustion? Measure the capacity of the bottle when filled up to the label. Supposing the atmosphere to consist of oxygen and nitrogen gases, what percentage by volume is oxygen? nitrogen?

(*c*) Nitrogen may be made by heating a conc. solution of ammonium nitrate ($NH_4NO_2 = N_2 + 2H_2O$); or by heating a mixture of potassium bichromate and ammonium chloride ($K_2Cr_2O_7 + 2NH_4Cl = 2KCl + Cr_2O_3 + 4H_2O + N_2$).

NITROUS OXIDE.

33. Heat 10 g. of ammonium nitrate in a large test-tube until the salt melts; then heat slowly, but continuously. Collect the gas over *warm* water. Why not over cold water? If any white fumes appear in making the gas, account for them. The gas thus prepared is nitrogen monoxide, or nitrous oxide (N_2O). Write the reaction.

(*a*) Insert a glowing splinter into a bottle of the gas.

(*b*) Burn some sulphur in a bottle of the gas. Does the sulphur burn exactly as sulphur in oxygen?

(*c*) Invert a bottle of the gas in a dish of cold water. If the gas does not all dissolve, test the residual gas with a glowing splinter.

(*d*) Incline a bottle of the gas standing over water until some bubbles of air enter. Is any change apparent?

Save a bottle of nitrous oxide for 34 (*e*).

NITRIC OXIDE.

34. Mix 5 cc. of water with 5 cc. of conc. HNO_3. Pour this diluted acid over 5 g. of copper turnings in a small flask. The reaction is $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$ (nitric oxide, or nitrogen dioxide). The formula is also written N_2O_2. Collect the gas over water.

(*a*) When several bottles of the gas have been collected let the remainder of the gas pass into a solution of ferrous sulphate ($FeSO_4$). The nitric oxide is absorbed by the solution to form $FeSO_4NO$.

(*b*) Incline a bottle of nitric oxide standing over water until a few bubbles of air enter. Nitrogen tetroxide is formed, written NO_2 or N_2O_4. Test with litmus paper the water in the bottle. $2NO_2 + H_2O = HNO_3 + HNO_2$. The nitrous acid ($HNO_2$) is at once decomposed at ordinary temperatures into nitric oxide and nitric acid. $3NO_2 + H_2O = 2HNO_3 + NO$.

Account for the red fumes which were at first seen in the test-tube in preparing nitric oxide. What became of them?

(*c*) Mix a small portion of the dark solution (*a*) with conc. H_2SO_4, keeping the mixture cool.

(*d*) Pour the remainder of the dark solution into a test-tube and heat. Is any gas given off?

(*e*) How can oxygen, nitrous oxide, and nitric oxide be distinguished from one another.

NITRIC ACID.

35 (*a*) Put 5 g. of sodium nitrate into a large test-

tube; cover it with conc. H_2SO_4; heat, collecting the distillate in a test-tube cooled in water. $2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$. Nitric acid is manufactured from these materials.

(*b*) Take 5 cc. cold dilute HNO_3 in a test-tube. Incline the test-tube and add carefully an equal volume of conc. solution of $FeSO_4$, so that the $FeSO_4$ solution will form a layer above the HNO_3. Set the tube aside. A dark ring should form where the liquids are in contact.

(*c*) Add to 3 cc. of a weak solution of any nitrate an equal volume of conc. H_2SO_4. Allow the mixture to cool. Now add conc. solution of $FeSO_4$ as in 35 (*b*). What is the test for a nitrate? Why should the mixture of H_2SO_4 and the solution to be tested for HNO_3 be cooled before the addition of the $FeSO_4$?

(*d*) Pour a few drops of conc. HNO_3 on some pieces of tin foil in a crucible. Wash the white powder obtained several times with water, decanting the liquid. Then place the white powder on a filter, and wash until the washings contain no HNO_3. (How can the absence of HNO_3 be proved?) Prove that the white powder is not a nitrate by applying the test for a nitrate. All nitrates are soluble in water. The tin is oxidized by the HNO_3. $4HNO_3 = 2H_2O + 2N_2O_4 + O_2$; $Sn + O_2 = SnO_2$

(*e*) Moisten a quill or other animal organic matter with conc. HNO_3. What color is imparted to it? Will ammonia remove the stain? Will water wash it out?

HYDROCHLORIC ACID.

36. (*a*) Put into a 300 cc. flask 20 g. of common salt, insert a funnel or thistle tube, which must reach nearly to the bottom of the flask, and connect the flask with three bottles, A, B, and C, B and C being half-full of water. Mark with a label the level of the water in B.

Pour 40 cc. of conc H_2SO_4 in the flask, and warm gently. Why do bubbles at first pass up through the water in B and C, and afterward do not appear in C? Disconnect A, connecting the generating flask with B.

(*b*) Test the gas in A by (1) holding near its mouth a drop of conc. ammonia suspended on the end of a glass rod, (2) inserting into the bottle a lighted splinter, (3) closing the mouth of the bottle and inverting it in water.

(*c*) Notice the level of the water in B. Test a portion of the solution in B by adding a few drops of silver nitrate. Is the white precipitate thus formed soluble in HNO_3?

(*d*) The reaction in making HCl is $NaCl + H_2SO_4 = NaHSO_4 + HCl$, or at a higher temperature $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$. In which of these reactions is the H_2SO_4 more economically used? Both reactions occur in making the HCl on a large scale.

Instead of using a funnel tube in the flask in the above experiment, the bottles B and C may each be provided with a third tube open at both ends, passing through the stopper and reaching below the surface of the liquid in the bottle.

AQUA REGIA, OR NITRO-HYDROCHLORIC ACID.

37. Mix 2 cc. of conc. HNO_3 with 6 cc. of HCl. This mixture is called *aqua regia*. It dissolves gold. It is also an excellent solvent for many other metals. The solution contains the chloride of the metal.

CARBON DIOXIDE.

38. Pour a little HCl into a test-tube containing a small quantity of sodium carbonate. Apply a lighted splinter to the mouth of the tube. Suspend in the tube a drop of clear lime-water on the end of a glass rod.

The gas given off is carbon dioxide $Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$ Would the same gas be evolved if other carbonates were used? other acids? Try some of them.

Put 20 g of marble ($CaCO_3$) in small pieces into a flask. Cover it with HCl. Collect the gas by downward displacement.

(*a*) Balance two beakers on a scale, and pour into one of them CO_2 from a bottle or beaker.

(*b*) Pour CO_2 from one beaker into another in which a wax taper is burning; into a beaker containing lime-water What is formed when CO_2 is conducted into lime-water. Try the effect of HCl on this precipitate

(*c*) Breathe through a glass tube into a beaker containing diluted lime-water. If the lime-water becomes cloudy, see if you can make it clear by continuing to pass into it air from the lungs What does this experiment prove?

(*d*) Conduct CO_2, passed through a little water to wash it, into 5 cc of blue litmus solution in a test-tube until the color of the solution is changed. Now warm the litmus solution, and observe the change of color. What does this experiment prove? State some of the properties of carbon dioxide gas. What is the test for a carbonate?

PART II.

EXPERIMENTS IN QUALITATIVE ANALYSIS.

THE METALS.

SEPARATION OF THE METALS INTO GROUPS.

39. Label twenty-four test-tubes as follows: Ag, Al, As′, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg′, Hg″, K, Mg, Mn, Na, (NH_4), Ni, Pb, Sb, Sn, Sr, and Zn. Place the tubes in a rack, and pour into each of them 5 cc. of a solution of a salt of a metal marked on the label.

(*a*) Add two or three drops of HCl to the liquid in each tube. If a precipitate forms, determine whether it is soluble in a larger quantity of the acid Group I. includes those metals which form chlorides insoluble in HCl. Which are they?

(*b*) Pour into each one of the tubes which contains a salt of a metal not belonging to Group I. 5 cc. of H_2S solution Add a larger quantity of the H_2S in cases in which there is an indication that a precipitate is forming. Group II. includes all those metals (exclusive of Group I) which are precipitated as sulphides in the presence of free acid. Which are they? Are the members of Group I. precipitated by H_2S in presence of free acid?

(*c*) To the remaining solutions add NH_4OH to neutralize the free acid (What salt of ammonia is formed? What does the NH_4OH form with the H_2S in solution?),

and then a few drops of yellow ammonium sulphide, $(NH_4)_2S_x$. If a precipitate forms, add more $(NH_4)_2S_x$. Group III. includes those metals which are not precipitated by H_2S in the presence of dilute acids, but by H_2S in alkaline solutions, or $(NH_4)_2S_x$ in neutral or alkaline solutions. Which metals belong to this group? Are there any members of Groups I. and II. precipitated by H_2S in alkaline solutions, or $(NH_4)_2S_x$ in neutral or alkaline solutions?

(*d*) To the remaining solutions add ammonium carbonate ($(NH_4)_2CO_3$) solution. If any of the carbonates thus precipitated are soluble in NH_4Cl, do not include them in Group IV. Group IV. includes those metals (exclusive of Groups I., II., and III.) which form with $(NH_4)_2CO_3$ carbonates insoluble in water or in NH_4Cl? Name them. Must the solution to which the $(NH_4)_2CO_3$ is applied for the separation of Group IV. have an acid or an alkaline reaction? Add $(NH_4)_2CO_3$ to an acidified solution of a salt of Group IV. Does $(NH_4)_2CO_3$ precipitate members of Groups I., II., and III.?

(*e*) Add sodium phosphate (Na_2HPO_4) to the remaining solutions. Group V. is thus separated. What does this group include? Does Na_2HPO_4 precipitate members of Groups I., II., III., and IV.?

(*f*) Group VI. embraces the metals still remaining in solution. Which are they?

Make out a table for the separation of a mixture of solutions of salts of the above metals into groups.

The student should now be required to determine what groups are represented in a mixture given to him. A group must be completely removed before the test for the following group is applied (?). How can it be determined that the group is completely removed? Boiling generally facilitates the formation and separation of a

precipitate; and the filtering also proceeds more rapidly when the liquid is hot.

GROUP I.

THE HYDROCHLORIC ACID GROUP.

40. (*a*) Add HCl to solutions of lead nitrate ($Pb(NO_3)_2$), silver nitrate ($AgNO_3$), and mercurous nitrate ($Hg'NO_3$). Test the solubility of the precipitates in boiling water. Test their solubility in ammonia. Add HCl to the solution in ammonia until the reaction is acid. Is all of the element reprecipitated?

(*b*) Test solutions of $Pb(NO_3)_2$, $AgNO_3$, $Hg'NO_3$, and mercuric chloride ($Hg''Cl_2$) with NaOH, H_2SO_4, potassium iodide (KI), potassium chromate (K_2CrO_4), and stannous chloride ($SnCl_2$), and record the results as indicated in the following table:

Reagent Added to.	$Pb(NO_3)_2$	$AgNo_3$.	$Hg'No_3$	$Hg''Cl_2$.	Soluble in (?).
NaOH					NaOH
H_2SO_4					NaOH
KI					KI
K_2CrO_4					K_2CrO_4
$SnCl_2$					HCl

(*c*) Heat in a dry ignition tube a small quantity of a mercury compound, a small quantity of the same compound mixed with Na_2CO_3.

(*d*) Heat on charcoal in the reducing flame of the blow-pipe AgCl (obtained as in *a*), $PbCl_2$, or $PbSO_4$. Are globules of Pb and Ag malleable? Can you cut them with a knife? Can you mark on paper with them?

Make out a scheme (from reactions in *a*) for the detection and separation of Pb, Ag, and Hg'. What confirmatory test could you apply for each?

How can a mercurous be distinguished from a mercuric salt? an iodide from a chromate?

The student should now be given exercises in the detection and separation of the elements in Group I.

GROUP II.

HYDROGEN SULPHIDE GROUP.

41. This group is divided into Sub-group A, metals whose sulphides are soluble in $(NH_4)_2S_x$, and Sub-group B, metals whose sulphides are insoluble (or nearly so) in $(NH_4)_2S_x$. Determine by experiment which metals belong to A. The precipitated sulphides of Group II. have generally the following composition: Sb_2S_3, As_2S_3, Bi_2S_3, CdS, CuS, PbS, HgS, SnS (brown), and SnS_2 (yellow).

SUB-GROUP A.

Sulphides Soluble in Ammonium Sulphide.

(*a*) Compare the solubility of Sn, Sb, As, SnO_2, Sb_2O_3, As_2O_3, SnS, Sb_2S_3, and As_2S_3 in boiling conc. HCl; in boiling conc. HNO_3. Record the results in tabular form. (The sulphides for this experiment may be gotten by precipitating stannous chloride ($SnCl_2$), antimonious chloride ($SbCl_3$), and arsenious chloride ($AsCl_3$) with H_2S, and washing the precipitate.) The best solvent for the metals is nitro-hydrochloric acid (41 *a*), or conc. HCl to which a crystal of $KClO_3$ is added, forming stannic chloride ($SnCl_4$), $SbCl_3$, and arsenic acid (H_3AsO_4)

(*b*) Compare the solubility of SnS, Sb_2S_3, and As_2S_3 in boiling conc. $(NH_4)_2CO_3$

(*c*) Put a piece of platinum foil in a porcelain dish and place on it a piece of zinc. Cover the Zn and Pt with a solution of $SnCl_2$. If the Zn is not acted upon, acidify with HCl until H is freely given off. Try a similar ex-

periment using $SbCl_3$ instead of $SnCl_2$. (This experiment *must not be tried with a compound of arsenic*, nor *in a mixture of these elements* until any *arsenic* that may be present *has been separated* from the mixture.)

Touch the platinum foil, if it be blackened, with a drop of conc. HNO_3 on the end of a glass rod; also touch it at another point with a drop of conc. HCl.

(*d*) Add $Hg''Cl_2$ to solutions of $SnCl_2$, $SbCl_3$, $AsCl_3$ (40 *b*).

(*e*) Blow a small bulb on the end of an ignition tube 10 cm. in length. Mix a small quantity of a *dry* compound of arsenic with six times its weight of a *dry* mixture of equal parts of Na_2CO_3 and potassium cyanide (KCN), place in the bulb, and heat The bulb should not be more than half-full of the mixture. If a mirror of arsenic forms in the upper part of the tube, break the tube and test the solubility of the arsenic in sodium hypochlorite (NaOCl). A mirror of the Sb is not soluble in this reagent.

(*f*) Mix a very small quantity of a compound of arsenic with Na_2CO_3 and KCN, and heat on charcoal in the reducing flame of the blow-pipe. Notice the odor of the fumes Heat in like manner an Sb compound, and when a globule is obtained throw the melted globule from the charcoal on the floor. Let another globule of Sb cool, and compare its color, solubility, and malleability with the corresponding properties of a globule of Sn gotten in the same way.

(*g*) Compare the action of H_2S on an arsen*ious* and an arsen*ic* compound; on a stan*nous* and a stan*nic* compound.

(*h*) Make some "Magnesia Mixture" by precipitating $MgSO_4$ solution with a large excess of NH_4OH, then adding NH_4Cl to the precipitate and solution until the pre-

cipitate is dissolved. Add "Magnesia Mixture" to sodium arsenite; to sodium arsenate; to sodium phosphate. Add $AgNO_3$ to a neutral solution of sodium arsenite; to sodium arsenate; to sodium phosphate Add ammonium molybdate solution to a few drops of sodium arsenite; to sodium arsenate; to sodium phosphate; and if, after a few minutes, no precipitate occurs, warm. How can arsenites, arsenates, and phosphates be distinguished from each other?

Can the precipitation of Sn, Sb, and As by H_2S be prevented by the presence of strong HCl? Which of these sulphides most readily dissolves in HCl? (41 *b*). Make out a scheme for the detection and separation of Sn, Sb, and As.

An exercise should be given in Sub-group A.

SUB-GROUP B.

Sulphides Insoluble in Ammonium Sulphides.

(*a*) Which members of Sub-group B are precipitated from solutions by H_2SO_4? by NH_4OH? Which sulphides of Group II. B are dissolved by boiling with HNO_3? by boiling with H_2SO_4? by KCN solution? Make out the results of these experiments in tabular form. From the above reactions make out a scheme for the separation of the members of Sub-group B.

(*b*) Dissolve the sulphide which is not soluble in HNO_3 in conc HCl to which a crystal of $KClO_3$ is added, boil off the chlorine and apply a test already known for the metal in solution.

(*c*) Add NH_4OH to a solution of $BiCl_3$. The precipitate is $Bi(OH)_3$. Dissolve this precipitate in as small a quantity of conc. HCl as possible. The solution contains bismuth chloride ($BiCl_3$). Dilute with water Bismuth oxychloride (BiOCl) is precipitated. Dilute with water

solutions of $BiCl_3$ and $SbCl_3$. Is either precipitate soluble in tartaric acid? The atmosphere sometimes precipitates stannous oxychloride (SnOCl) from solutions of $SnCl_2$ on standing. How could this be distinguished from the oxychlorides of Bi and Sb?

(*d*) Heat Bi_2S_3 on charcoal before the blow-pipe. Test in like manner CdS.

(*e*) Sulphur formed by the decomposition of H_2S or $(HN_4)_2S_x$ may be mistaken for a metallic sulphide. It may be recognized by the tests (28 *a*). Add an acid to H_2S. Add an acid to $(NH_4)_2S_x$. Add H_2S to K_2CrO_4. Add H_2S to Fe_2Cl_6. CuS is slightly soluble in warm $(NH_4)_2S_x$, but not in sodium hydrosulphide (NaSH); but HgS is somewhat soluble in the latter. Hence in the absence of Hg, NaSH is sometimes used instead of $(NH_4)_2S_x$ for the separation of the sulphides of Sub-group B from those of Sub-group A. Sodium hydrosulphide is made by saturating a solution of NaOH with H_2S.

An exercise should be given in Sub-group A; also one in a mixture of Sub-groups A and B, or in a mixture of Groups I. and II.

GROUP III.

AMMONIUM SULPHIDE GROUP.

42. (*a*) Heat Co, Mn, and Ni compounds in the borax bead. Heat a Mn compound with a mixture of Na_2CO_3 and $NaNO_3$ on platinum foil. Heat a Zn compound moistened with cobalt nitrate on platinum foil. Heat an Al compound strongly on charcoal, moisten with a solution of cobalt nitrate and heat again. Try a like experiment with calcium phosphate (Ca_3PO_4)

(*b*) Place in test-tubes 5 cc. each of the nitrates, chlorides, or sulphates of Al, Co, Cr, Fe′, Fe″, Mn, Ni, Zn. Add NH_4OH. The hydroxides are formed, $Al_2(OH)_6$,

$Co(OH)_2$, $Cr_2(OH)_6$, $Fe(OH)_2$, $Fe_2(OH)_6$, $Mn(OH)_2$, $Ni(OH)_2$, $Zn(OH)_2$. Which are dissolved in excess of NH_4OH? Which are soluble in NH_4Cl, and consequently not precipitated in the presence of a sufficient quantity of NH_4Cl? Is $Fe(OH)_2$ at all soluble in NH_4OH?

(*c*) Test $FeSO_4$ and Fe_2Cl_6 separately with NH_4OH, with potassium ferrocyanide (K_4FeCy_6), and with potassium sulphocyanate (KCNS). Boil $FeSO_4$ with a few drops of strong HNO_3 until the solution changes color; then test portions of it with NH_4OH, K_4FeCy_6, KCNS

(*d*) Add solution of lead acetate to a solution of K_2CrO_4. Add solution of $AgNO_3$ to a solution of K_2CrO_4. Mix $Cr_2(OH)_6$ (see its formation above) with $NaNO_3$ and Na_2CO_3; treat the fused mass with water, acidify with acetic acid, and test the solution with lead acetate, with $AgNO_3$. How can a compound insoluble in water be tested for Cr?

(*e*) To solutions of nitrate, chloride, or sulphate of Al, Cr, Fe′ add slowly NaOH. The hydroxides are precipitated. Which of these precipitates dissolve in excess of NaOH in the cold? Do any dissolve on boiling? Are any that dissolve in the cold reprecipitated by boiling? by adding NH_4Cl? How can Al, Cr, and iron in a mixture be separated, and the presence of each be shown, the iron being in a ferric condition? the iron being in a ferrous condition? Try the latter.

(*f*) To nitrates, chlorides, or sulphates of Co, Mn, Ni, and Zn add $(NH_4)_2S$. The precipitates are CoS, MnS, NiS, and ZnS. Note their color. Which are soluble in HCl? acetic acid? nitro-hydrochloric acid?

(*g*) Add NaOH to solutions of Co, Mn, Ni, and Zn The hydroxides $Co(OH)_2$, $Mn(OH)_2$, $Ni(OH)_2$, $Zn(OH)_2$ are formed. Are any of these precipitates soluble in NaOH?

(*h*) To 5 cc. cobaltous chloride ($CoCl_2$) add solution of KCN gradually. The precipitate is cobaltous cyanide ($Co(CN)_2$). On adding an excess of KCN the precipitate dissolves, and the solution contains the double salt, potassium cobalto-cyanide ($K_4Co(CN)_6$), analogous to potassium ferro-cyanide ($K_4Fe(CN)_6$): $Co(CN)_2 + 4KCN = K_4Co(CN)_6$. Add *one* or *two* drops of HCl to the solution, heat it nearly to the boiling point, and allow it to stand for five minutes. Then to a portion of the solution add excess of HCl; to the other portion add NaOH in large excess, warm gently, and add bromine water

(*i*) The same as (*h*) using nickelous chloride ($NiCl_2$) instead of $CoCl_2$.

In (*h*) if instead of *one* or *two* drops of HCl the solution be neutralized or acidified *without heating*, the potassium cobalto-cyanide is decomposed, and $Co(CN)_2$ is precipitated But when only a few drops of the acid are added (the KCN remaining in excess) and the solution is heated the free hydrocyanic acid (HCN) converts the $Co(CN)_2$ into cobaltic cyanide ($Co_2(CN)_6$), which unites with KCN to form potassium cobalti-cyanide ($K_3Co(CN)_6$), analogous to potassium ferri-cyanide ($K_3Fe(CN)_6$). $KCN + HCl = KCl + HCN$; $2HCN + 2Co(CN)_2 = H_2 + Co_2(CN)_6$, $Co_2(CN)_6 + 6KCN = K_6Co_2(CN)_{12}$, or $2K_3Co(CN)_6$ $K_3Co(CN)_6$ *is not decomposed* by dilute acids and *is not precipitated* by warming with excess of NaOH and adding bromine water.

Potassium nickelous-cyanide ($K_4Ni(CN)_6$) in presence of KCN is not converted by the action of HCl into a compound corresponding to potassium cobalto-cyanide, but *is decomposed*, and $Ni(CN)_2$ precipitated (?). When NaOH in large excess is added to a solution of $K_4Ni(CN)_6$ and the mixture is then warmed gently and bromine water added, nickelic hydroxide ($Ni(OH)_3$) *is precipitated* (?).

$K_4Ni(CN)_6 + 13Br + 3KOH = 7KBr + Ni(OH)_3 + 6BrCN$. The precipitate should be tested for Ni by means of the sodium metaphosphate bead

CoS and NiS are converted into $CoCl_2$ and $NiCl_2$ by dissolving in nitrohydrochloric acid. Before adding KCN evaporate the above solution almost to dryness and dissolve in water, adding a few drops of HCl if necessary for solution.

Take a mixture of $CoCl_2$ and $NiCl_2$, precipitate with $(NH_4)_2S_x$, and see if you can prove the presence of Co and Ni by the above process.

Make out a scheme for the separation and detection of Al, Co, Cr, Fe′, Fe″, Mn, Ni, and Zn in mixtures.

An exercise should be given in Group III.

PRECAUTIONS IN THE SEPARATION OF GROUPS I., II., AND III.

43. Perform the following experiments, and then state what precautions are necessary in the separation of the members of Group III. from the filtrate of Group II

(*a*) Boil 1 cc. Fe_2Cl_6 with H_2S, and then determine whether the iron is in a ferrous or a ferric state (42 *c*).

(*b*) Boil a solution of H_2S; test the gas coming off with a piece of paper moistened with lead acetate. When paper moistened with lead acetate is not blackened by holding it to the mouth of the test-tube test the solution with lead acetate (39 *c*).

(*c*) Add NH_4OH to a solution of $MgSO_4$. Add NH_4Cl to a solution of $MgSO_4$ and then add NH_4OH (39 *c*).

GROUP IV.

AMMONIUM CARBONATE GROUP.

44. (*a*) What colors do salts of Ba, Ca, Sr, and Cu give when moistened with HCl and held in the flame on the end of a platinum wire?

(*b*) To solutions of $BaCl_2$, $CaCl_2$, and $SrCl_2$ add the following reagents (test the delicacy of the reaction when a precipitate is given by diluting to a large volume):

Reagent.	$BaCl_2$.	$CaCl_2$.	$SrCl_2$.	
$CaSO_4$.				
H_2SO_4.				Completely precipitated (?).
H_2SO_4 + alcohol.				
Hydro-fluosilicic acid (H_2SiF_6).				
H_2SiF_6 + alcohol.				
NH_4OH + NH_4Cl + Ammonium oxalate ($(NH_4)_2C_2O_4$)				Is the test most delicate for Ba, Ca, or Sr?
K_2CrO_4.				Soluble in acetic acid (?).

Are Mg salts precipitated by the reagents used in the above table? Are Ba, Ca, and Sr completely precipitated by NH_4OH, NH_4Cl, and $(NH_4)_2CO_3$ from solutions of their salts?

How can Ba, Ca, and Sr be completely removed from a solution containing Ba, Ca, Sr, and Mg, leaving the Mg in solution?

(*c*) Test the solubility of finely powdered chlorides and nitrates of Ba, Ca, and Sr in absolute alcohol, cold and warm Use very small quantities. The chlorides

and nitrates may be made from the precipitated carbonates by dissolving the carbonates in as little HCl or HNO_3 as possible, evaporating to dryness, taking up in a little water and evaporating again.

(*d*) Are members of Group I., II., and III. precipitated by NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$? Make out a scheme for the separation and detection of Ba, Ca, and Sr in mixtures

An exercise should be given on Group IV.

GROUP V.

SODIUM PHOSPHATE GROUP.

45. (*a*) Heat a magnesium salt on charcoal before the blow-pipe; moisten with a solution of $Co(NO_3)_2$, and heat again.

(*b*) To a solution of magnesium sulphate ($MgSO_4$) add NH_4Cl, NH_4OH, and sodium phosphate (Na_2HPO_4) Try this test with a *very* dilute solution of $MgSO_4$. Rubbing the inside of the test-tube with a glass rod will facilitate the separation of the precipitate. The precipitate is $Mg(NH_4)PO_4$

(*c*) Add barium hydroxide $Ba(OH)_2$ to a solution of $MgCl_2$. The precipitate is magnesium hydroxide ($Mg(OH)_2$). It is somewhat soluble in ammonium salts (?) What remains in solution?

GROUP VI

SOLUBLE GROUP.

46. (*a*) Test salts of NH_4, K, and Na on a platinum wire in the flame. Examine the flame in each case by looking through a piece of blue glass. Mix the three compounds and examine in the flame without the glass; through the glass

(*b*) Are NH_4, K, and Na salts volatile at a faint red heat? Heat them on platinum foil.

(*c*) Rub salts of NH_4, Na, and K with caustic lime moistened with water. Notice the odor.

(*d*) Add one or two drops of platinum chloride ($PtCl_4$) to neutral or acid solutions of NH_4, Na, and K salts on watch-glasses. Examine the precipitates with a microscope.

(*e*) Add tartaric acid to neutral solutions of NH_4, Na, and K salts; to alkaline solutions.

(*f*) Prove the presence of NH_4, K, and Na in a mixture of solutions of NH_4Cl, KCl, and NaCl

SEPARATION OF GROUPS IV., V., AND VI.

47. Take a mixture of $BaCl_2$, $MgCl_2$, and KCl. Add NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$. Filter. To filtrate add a few drops of H_2SO_4 What is the slight precipitate? Filter. What remains in solution in the filtrate? Remove ammonium salts from the filtrate by evaporating and heating to faint redness. Dissolve the residue in water and add excess of $Ba(OH)_2$ What is the precipitate? What remains in solution? Add NH_4OH and $(NH_4)_2CO_3$. What is the precipitate? Filter. What is in the filtrate? Evaporate the filtrate and heat to redness. For what purpose? Test the residue in the flame. Dissolve the residue in water, adding a few drops of HCl to convert any K_2CO_3 that may have been formed into KCl. Add $PtCl_4$ to the solution. Examine the precipitate with a microscope.

Make out a scheme for the separation of Mg, K, and Na from Group IV. and for proving their presence.

An exercise should be given with a mixture of salts of Groups IV., V., and VI. An exercise should be given with a mixture containing any or all of the Groups.

SOME SPECIAL CASES UNDER GROUP III.

Ba, Ca, Sr may be precipitated in Group III. when present in the form of phosphate, silicate, fluoride, borate, or oxalate. As an example of this we give calcium phosphate ($Ca_3(PO_4)_2$).

48. Dissolve 5 g $Ca_3(PO_4)_2$ in HCl Divide the solution into three portions, *a*, *b*, and *c*. To *a* add NH_4OH to alkaline reaction. Dissolve the precipitate in HNO_3 and test for H_3PO_4 with ammonium molybdate. Dilute *b* with ten volumes of water. To a small portion of this solution add H_2SO_4, then three volumes of alcohol. This suggests a method for the detection of Ca, Ba, and Sr when precipitated as phosphates in Group III. Another method is indicated by the following experiment: Almost neutralize *c* with NaOH; add an equal volume of sodium acetate, and then a few drops of acetic acid Now add Fe_2Cl_6 drop by drop as long as a precipitate forms and until the liquid after shaking remains reddish. Heat to boiling and filter hot. The precipitate should contain the H_3PO_4 as phosphate of iron; the filtrate, the Ca as $CaCl_2$. Test the precipitate for H_3PO_4 and the filtrate for Ca.

THE ACIDS.

INORGANIC ACIDS

BARIUM CHLORIDE GROUP.

49. Add $BaCl_2$ to the following acids made neutral with NH_4OH, or to neutral solutions of soluble salts containing these acids, and determine which of the precipitates are soluble in HCl: acetic, arsenious, arsenic, benzoic, boric, carbonic, chloric, chromic, citric, formic, hyposulphurous, hyposulphuric (hydrogen sulphide), hydrobromic, hydrochloric, hydriodic, hydroferrocyanic,

hydroferricyanic, hydrofluoric, nitric, oxalic, phosphoric, sulphurous, sulphuric, and tartaric.

Of the above acids acetic, benzoic, carbonic, oxalic, and tartaric are organic.

SILVER NITRATE GROUP.

50 (*a*) Add a few drops of $AgNO_3$ to neutral solutions of salts of the acids mentioned in 49. Note the color of each precipitate. Which of the precipitates are soluble in HNO_3? in NH_4OH? in excess of the solution to which the $AgNO_3$ is added? Compare the results of 49 and 50 (*a*).

(*b*) Put a crystal of KCl in a test-tube, add a little black oxide of manganese (MnO_2), and then a few drops of conc. H_2SO_4 Heat cautiously Notice the color of the gas that is given off Try what effect the gas has upon the color of some starch paste placed on the end of a glass rod, or dissolved in water. Test KBr and KI in the same way as KCl.

(*c*) Test potassium ferrocyanide with $FeSO_4$ solution; with a solution of Fe_2Cl_6. Test potassium ferricyanide with $FeSO_4$ solution; with a solution of Fe_2Cl_6. Add a few drops of Fe_2Cl_6 to a solution of $FeSO_4$; then add some NaOH, and warm. Is the precipitate soluble in HCl? To a solution of potassium cyanide (KCN) add $FeSO_4$, a few drops of Fe_2Cl_6, NaOH, warm; then add HCl.

SILICIC ACID (H_4SiO_4).

51. Acidulate a solution of sodium silicate with HCl, and evaporate to dryness on the water bath. Treat the residue with water and HCl, and again evaporate to dryness. Silica (SiO_2) insoluble in HCl should remain. Heat a particle of SiO_2 in the sodium metaphosphate bead.

Insoluble silicates can be converted into alkaline sil-

icates by fusing with four parts of mixed carbonates of potassium and sodium.

HYDROFLUORIC ACID (HF).

52 Coat a watch-glass with paraffin. Trace a figure in the paraffin, cutting the lines down to the glass. Mix 1 g. CaF_2 in a lead crucible with conc. H_2SO_4 to form a thin paste. Cover the crucible with the coated watch-glass, and let it stand for half an hour in a warm place. Remove the wax from the watch-glass. The figure is etched on the glass (?).

BORIC ACID (H_3BO_3).

53. (*a*) With a solution of a borate form precipitates by means of $BaCl_2$, $CaCl_2$, $AgNO_3$, and lead acetate. What are these precipitates soluble in?

(*b*) Mix some borax in a porcelain dish with conc. H_2SO_4, cover it with alcohol and ignite. Stir the mixture while it is burning and notice the color imparted to the flame. Try a similar experiment, omitting the H_2SO_4. Vary the experiment by using boric acid instead of borax, and omitting the H_2SO_4. Moisten borax with conc. H_2SO_4 and heat in the loop of a platinum wire in the oxidizing flame. Let the bead cool; moisten it with glycerin, and heat again. What other substances color the flame green?

(*c*) Make a solution of a borate slightly acid with HCl, dip into it a slip of turmeric paper, and dry the paper at a gentle heat.

SULPHUROUS ACID (H_2SO_3); HYPOSULPHUROUS (THIOSULPHURIC) ACID ($H_2S_2O_3$).

54. To solutions of sodium sulphite (Na_2SO_3) and sodium hyposulphite ($Na_2S_2O_3$ add (1) HCl; (2) $AgNO_3$ gradually; (3) Fe_2Cl_6; (4) $CaCl_2$.

CHLORIC ACID ($HClO_3$).

55. (*a*) Heat a crystal of $KClO_3$ before the blow-pipe on charcoal.

(*b*) Mix a *very small* quantity of $KClO_3$ with KCN, and heat on platinum foil.

(*c*) Let fall a few drops of conc. H_2SO_4 on a crystal of $KClO_3$ in a test-tube. Warm gently. (Caution.)

ORGANIC ACIDS.

TEST OF AN ORGANIC COMPOUND.

56. (*a*) The blackening of a substance on heating in an ignition tube usually indicates the presence of an organic acid Heat in this way potassium tartrate, potassium citrate, sodium acetate.

(*b*) Blackening without charring may be due to the formation of a black oxide, and may take place when no organic acid is present Heat $Cu(NO_3)_2$ in an ignition tube or on platinum foil.

The presence of certain organic acids prevent or retard the precipitation of some of the bases by the group reagents, hence it is best in making an analysis to remove or destroy organic acids by combustion as above, or by other methods given in works on qualitative analysis, before applying the group reagents.

The organic acids are very numerous. The experiments here will be limited to oxalic, tartaric, citric, malic, succinic, benzoic, formic, and acetic acids.

CONC. H_2SO_4 ON ORGANIC ACIDS.

57. Pour conc. H_2SO_4 on small quantities of salts of the above acids in test-tubes. Observe what takes place. After a few minutes, heat. Oxalic and formic acids are decomposed as follows: $C_2H_2O_4 = H_2O + CO_2 + CO$;

$CH_2O_2 = H_2O + CO$. Carbonic oxide (CO) burns with a blue flame. Test for it at the mouth of the test-tube

OXALIC, TARTARIC, CITRIC, AND MALIC ACIDS.

58. To neutral solutions of salts of these acids add:

(*a*) $CaCl_2$. The precipitates are soluble in acetic acid (?). The precipitates dissolve in cold KOH (?), and fall again on boiling the solution (?).

(*b*) Lime-water in considerable quantity; if no precipitate appears, boil.

(*c*) Lead acetate. The precipitates are soluble in NH_4OH (?).

SUCCINIC, BENZOIC, FORMIC, AND ACETIC ACIDS.

59. To solutions of salts of these acids add:

(*a*) Fe_2Cl_6, boil; treat the precipitates with NH_4OH; then add conc. HCl in excess.

(*b*) A mixture of alcohol, NH_4OH, and $CaCl_2$.

(*c*) $HgNO_3$; boil.

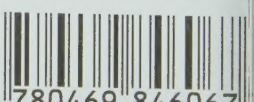
(*d*) Warm a crystal of sodium acetate with conc. H_2SO_4 and an equal volume of alcohol. Acetic ether is formed. Notice the odor of it.

ORGANIC COMPOUNDS INSOLUBLE IN WATER.

To detect an organic acid in a compound insoluble in water the compound is first decomposed by boiling with a solution of Na_2CO_3. The organic acid goes into solution in the form of a sodium salt.

60 Boil calcium oxalate (obtained by adding ammonium oxalate to $CaCl_2$) with Na_2CO_3 solution. Filter. Neutralize the filtrate with acetic acid, and test for oxalic acid with $CaCl_2$. Why is acetic acid used instead of HCl? How is calcium oxalate distinguished from calcium tartrate? from calcium phosphate?

Lightning Source UK Ltd.
Milton Keynes UK
UKHW021137300621
386402UK00005B/906



This work has been selected by scholars as being culturally important, and is part of the knowledge base of civilization as we know it. This work was reproduced from the original artifact, and remains as true to the original work as possible. Therefore, you will see the original copyright references, library stamps (as most of these works have been housed in our most important libraries around the world), and other notations in the work.

This work is in the public domain in the United States of America, and possibly other nations. Within the United States, you may freely copy and distribute this work, as no entity (individual or corporate) has a copyright on the body of the work.

As a reproduction of a historical artifact, this work may contain missing or blurred pages, poor pictures, errant marks, etc. Scholars believe, and we concur, that this work is important enough to be preserved, reproduced, and made generally available to the public. We appreciate your support of the preservation process, and thank you for being an important part of keeping this knowledge alive and relevant.

Published by Wentworth Press, an imprint of Creative Media Partners.
support.creativemedia.io

W8-BTP-807